

## Article

# Synthesis of Multi-butylnaphthalene Base Oils Catalyzed by Trifluoromethanesulfonic Acid and Its Lubricating Properties

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**Abstract:** Alkylnaphthalene as base oils are widely applied in the production of high-performance lubricating oils. Here, we report the synthesis of multi-butylnaphthalenes by alkylation of naphthalene and *n*-butene with trifluoromethanesulfonic acid as catalyst. Trifluoromethanesulfonic acid exhibited excellent catalytic performance with naphthalene conversion, as high as 98.5%, and the multi-butylnaphthalenes selectivity of 98.8% under optimum conditions. To investigate the effects of the side-chain numbers on naphthalene on the lubrication performance, two kinds of alkylnaphthalenes were obtained by controlling catalyst dosage, denoted as MBN-1 (90.3% mono/di-butylnaphthalenes) and MBN-2 (98.2% tri/tetra/penta/hexa-butylnaphthalenes), respectively. The primary physiochemical properties of the synthetic oils were tested, and their tribological performance was evaluated. MBN-2, with more side chains on naphthalene, displayed more effective friction reduction and anti-wear properties than MBN-1 and the commercial alkyl naphthalene base oil AN5.

**Keywords:** naphthalene; trifluoromethanesulfonic acid; alkylation; synthetic lubricating base oil

## 1. Introduction

Alkylnaphthalene was one of the important alky aromatic lubricating base oils for production of high-performance lubricating oils and greases [1,2]. Alkylnaphthalene, as a lubricating base oil, displayed excellent properties, such as anti-oxidation stability, thermal stability, hydrolysis stability, and anti-emulsification properties. This was due to its own aromatic ring structure and the connected side chain alkyl, which could be used as automotive engine oil, heat transfer oil, and grease base oil [3,4].

Alkylnaphthalene lubricating oils were mainly produced through the alkylation of olefins and naphthalene with acid as catalyst [5,6]. The properties of alkylnaphthalene were closely associated with the structure and number of side chain alky groups on naphthalene. In particular, the increase in alkyl chain length and the number of alkyl chain on the naphthalene ring enhanced the intermolecular force, which usually resulted in the alkylated naphthalene having higher viscosity, pour point, oxidation onset temperature, and flash point. Additionally, the low aniline point was proposed to be related to the proportion of polar naphthalene ring increased from the samples [7]. As a lubricating base oil, alkylated naphthalene should have excellent conditions and life in storage, transport, and operation; thus, it was necessary to improve its thermal oxidation stability, low temperature fluidity, and additive solubility. Furthermore, the wear as an important factor must be reduced to prolong the life and enhance efficiency of a machine system [4]. In our group, we applied ionic liquid as acid catalysts for the alkylation of naphthalene or other aromatic hydrocarbons with long chain  $\alpha$ -olefins (C6-C8) to synthesize high viscosity lubricating base oils [8–10]. Among them, alkylnaphthalene oils exhibited outstanding thermal stability and oxidation stability as lubricating base oils; however, their high pour points were not beneficial to the application at low temperature conditions. Regarding the long-chain  $\alpha$ -olefins, the steric hindrance of alkylnaphthalene significantly affected the side-chain alkyl numbers on the naphthalene ring, leading to the difficulty in controlling the properties of the resulting products.



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Heterogeneous catalysts had been commonly utilized as catalysts for alkylation, such as metal oxides [11], molecular sieves [12,13], and acidic resins [14]. Although such catalysts had good catalytic performance, the catalytic activity usually decreased as the catalyst deactivated by carbon deposition at the high reaction temperature. We used ionic liquids (ILs) to catalyze the alkylation of aromatic hydrocarbons with  $\alpha$ -olefins, and they exhibited excellent catalytic performance [15–17]. However, the synthetic process of ILs was complicated, and ILs were very sensitive to water and the oxygen-containing compounds in feedstock that often led to the deactivation of the catalyst [18]. Furthermore, ILs probably interacted with aromatics to form the undesired compounds during the reaction, which would buffer the acidity at a lower level and slow down the alkylation process [19]. In addition, the other homogeneous catalysts were also widely used in alkylation, which were widely applied in industrial production due to their small catalyst dosage and low reaction temperature [20,21]. As an organic superacid, trifluoromethanesulfonic acid (TfOH) exhibited good stability, and high activity for alkylation reaction under mild reaction conditions, and had the advantages of strong acidity and low cost [22]. Song et al. [23] demonstrated the excellent catalytic performance of TfOH in the alkylation of naphthalene with long  $\alpha$ -olefins. The conversion of naphthalene reached more than 96%, and the selectivity of multi-alkylnaphthalene was high, and the synthesized alkylated naphthalene could be used as lubricating base oils. Wang et al. [24] found that the alkylation process using TfOH as a catalyst could achieve continuous operation, and the obtained alkyl naphthalene had high yield and good stability. Therefore, TfOH could be used as an efficient catalyst for naphthalene alkylation.

With the large-scale production of catalytic cracking of petroleum and the maturity of methanol-to-olefins, a large amount of C4 olefins had been produced as the product [25,26]. *n*-Butene was mainly produced from the separation of C4 fractions, and the output and quality of *n*-butene had also improved significantly as chemical technology improved [27,28]. As an important chemical product, *n*-butene was mainly used as a raw material for PE copolymer monomer and other chemical products, but it was gradually replaced by 1-hexene, 1-octene. This resulted in a surplus of *n*-butene; therefore, there was an urgent need to find new downstream products for the high value-added utilization of *n*-butene [29]. Herein, the synthesis of alkylnaphthalene was studied by alkylation of naphthalene with *n*-butene instead of long chain olefins. The typical acid catalyst of trifluoromethanesulfonic acid (TfOH) was applied for such reaction, and the effects of catalyst dosage, reaction temperature, flow rate of *n*-butene and reaction time on the reaction results were investigated in detail. The two isolated butylnaphthalene oils with various side chain number on naphthalene ring were evaluated as lubricating base oils to reveal the structure-performance relationship.

## 2. Materials and Methods

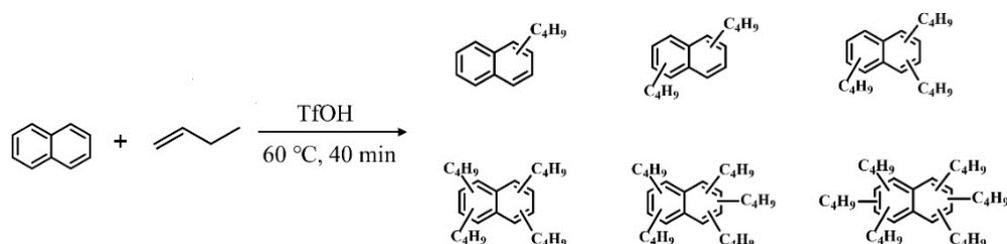
### 2.1. Materials

Naphthalene (C<sub>10</sub>H<sub>12</sub>, 99%), trifluoromethanesulfonic acid (CF<sub>3</sub>SO<sub>3</sub>H, 98%) and *n*-decane (C<sub>10</sub>H<sub>22</sub>, 98%) were purchased from Aladdin. *n*-butene (C<sub>4</sub>H<sub>8</sub>, 99.2%) was obtained from Henan Xingdao Gas Technology Co., Ltd. (Zhengzhou, China). All the reagents were used as received without further purification. The alkylnaphthalene base oil (AN5) was purchased from Shanghai NACO Lubrication Co., Ltd. (Shanghai, China).

### 2.2. Synthesis and Products Analysis

Two samples of alkylated naphthalene with different compositions, denoted as MBN-1 and MBN-2, were synthesized by regulating the reaction conditions. The sample MBN-2 was synthesized under the following conditions: 6.5 g of *n*-decane, 1.9 g of naphthalene, and 3.2 wt% of TfOH were added into the flask. When the temperature reached 60 °C, the *n*-butene bubbled under the solution level through a glass tube. The flow rate of the *n*-butene was 20 mL/min, which was controlled by the calibrated rotameter for 60 min. In order to reduce the loss of the *n*-butene, a glass tube was connected with the condenser and the other side of the flask. The finish of the *n*-butene, the system was stirred at 500 rpm

for an additional 40 min to make the alkylation completely, a series of alkylated products were obtained (Scheme 1). The MBN-1 was synthesized at 0.8 wt% of TfOH dosage and other conditions were the same as above.



**Scheme 1.** The alkylation of naphthalene with *n*-butene.

Then, the reactor was cooled down to room temperature, and the mixture was washed with a saturated  $\text{Na}_2\text{CO}_3$  solution to remove the residual catalyst remaining in the product. The solvent and the remaining small amount of naphthalene were removed by vacuum distillation, and the residue mixture was obtained as multi-butyl naphthalenes.

The conversion of naphthalene and the distribution of product were analyzed using a gas chromatograph GC-2010 Pro (equipped with a DB-5HT column:  $15\text{ m} \times 0.25\text{ mm} \times 0.10\text{ }\mu\text{m}$ ) and gas chromatography-mass spectrometry GC-MS QP2010Ultra (equipped with a Rtx-5MS column:  $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$ ) from Shimadzu (Japan). The temperature program of chromatographic was as follows: the initial column temperature was maintained at  $50\text{ }^\circ\text{C}$  for 2 min, then raised to  $200\text{ }^\circ\text{C}$  at  $15\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  that retained for 2 min, then increased to  $280\text{ }^\circ\text{C}$  at  $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ , and maintained for 3 min.

The peak area of naphthalene was derived from the GC as shown in Figure S1. The conversion of naphthalene was quantified by external standard method, and the standard curve of naphthalene was shown in Figure S2. Since the standard of products was difficult to obtain, the selectivity of the products was calculated by area normalization method.

### 2.3. Physicochemical Properties Test

The kinematic viscosities at  $40\text{ }^\circ\text{C}$  ( $\text{KV}_{40}$ ) and  $100\text{ }^\circ\text{C}$  ( $\text{KV}_{100}$ ) were measured using a BSY-108 Kinematic viscosity tester (Dalian Beigang) according to the method of ASTM D445; the density at  $20\text{ }^\circ\text{C}$  was determined using a DMA 1001 density meter (Anton Paar) according to the ASTM D4052 method; the flash point was measured using a CLA 5 flash point tester (Anton Paar) according to the ASTM D92 method; the pour point was measured using a SYD-510F1 multifunctional low-temperature tester (Shanghai Changji) according to the GB/T 3535 method; the aniline point was tested using an SYD-262A aniline point tester (Shanghai Changji) according to the GB/T 262 method; the oxidation onset temperature was determined using a DSC 204HP pressure differential scanning calorimetry (Netzsch) according to the SN/T 3950 method, and the test conditions was heated at a rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  under ambient pressure and oxygen flow rate of  $100\text{ mL}\cdot\text{min}^{-1}$ .

### 2.4. Tribological Tests

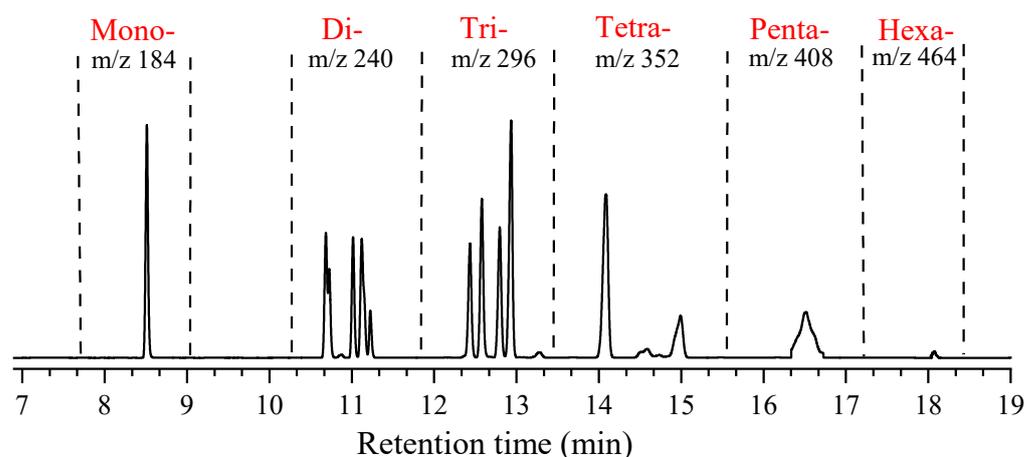
The tribological performance of the synthetic oils was evaluated by an Optimol SRV-V oscillating reciprocating friction and wear tester (Germany) according to the ASTM D6425 method. During the test, the AISI 52100 steel ball ( $\varphi$ : 10 mm, hardness: 59–64 HRC) is rubbed against the AISI-52100 steel plate ( $\varphi$ : 24 mm, hardness: 59–61 HRC, thickness: 7.9 mm). The main conditions were as follows: sample volume of 0.3 mL, temperature of  $25\text{ }^\circ\text{C}$ , frequency of 50 Hz under the load of 100 N, and stroke of 1 mm for 1800 s duration. After the test, the corresponding profile of the wear scars and wear volumes of the synthetic oils on the steel disc were observed by a 3D non-contact surface profiler (Zygo, Zegage).

### 3. Results and Discussions

#### 3.1. The Alkylation of Naphthalene and *n*-butene

The alkylation of naphthalene with *n*-butene was a typical Friedel-Crafts reaction. The alkylated naphthalene products were confirmed by GC-MS method. The analysis showed that mono-, di-, tri-, and tetra-butylnaphthalene had the same molecular ion peak with a mass-to-charge ratio of 155, which was  $C_{10}H_8-C_2H_4^+$  ( $C_2H_4^+$  bonded to  $C_{10}H_8$ ). Additionally, penta- and hexa-butylnaphthalenes had the same molecular ion peak with a mass-to-charge ratio of 253, which was  $2C_4H_9-C_{10}H_8-CH_2^+$ , as shown in Figure S3.

As shown in Figure 1, it was concluded that the compositions of products were mono-, di-, tri-, tetra-, penta-, and hexa-butylnaphthalene and their isomers owing to the rearrangement of carbocations and multiple substitution sites on the naphthalene ring.



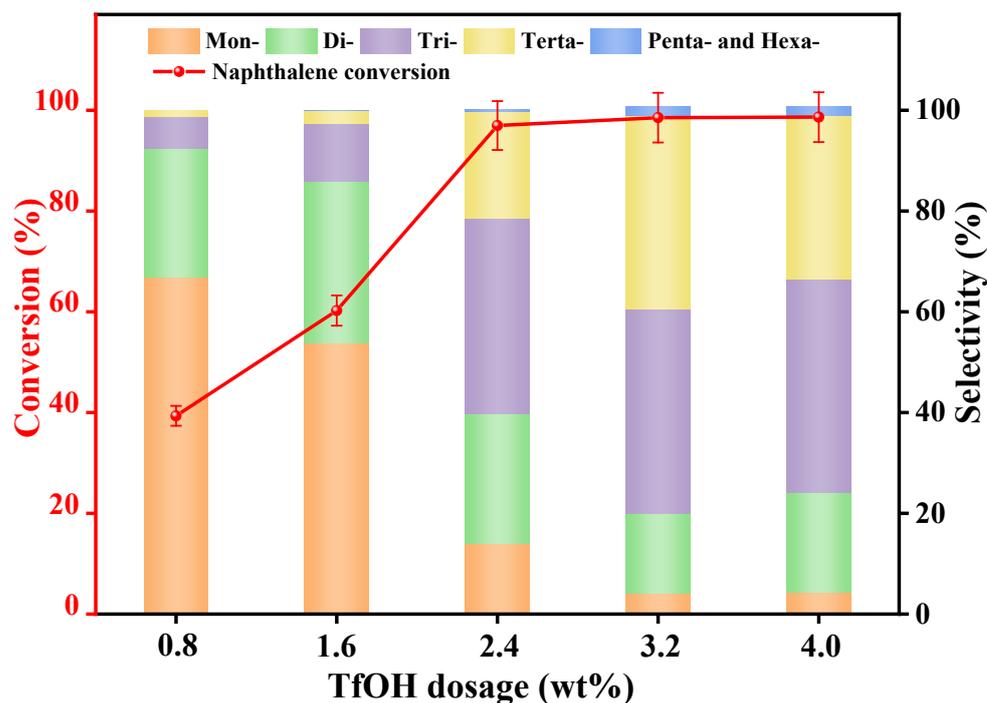
**Figure 1.** The GC spectra of butylnaphthalenes. Mono-: mono-butylnaphthalenes; Di-: di-butylnaphthalenes; Tri-: tri-butylnaphthalenes; Tetra-: tetra-butylnaphthalenes; Penta-: penta-butylnaphthalenes; Hexa-: hexa-butylnaphthalenes; m/z: mass-to-charge ratio.

#### 3.2. Effect of Reaction Conditions

There were many factors that affected the conversion of naphthalene and product distribution, and the influence of different reaction conditions on the alkylation of naphthalene with *n*-butene was explored in detail, such as catalyst dosage, reaction temperature, flow rate of *n*-butene, and reaction time.

##### 3.2.1. Catalyst Dosage

In the presence of TfOH, the effect of catalyst dosage on the alkylation reaction with naphthalene and *n*-butene was first investigated, as shown in Figure 2. Overall, the conversion of the naphthalene and the selectivity of the multi-butylnaphthalenes (tri-, tetra-, penta-, and hexa-butylnaphthalenes) were increased with an increasing dosage of TfOH, and when the addition amount was more than 3.2 wt%, the improvement was implicit because of steric hindrance effect of naphthalene. As the process was a tandem reaction, the formation of the multi-butylnaphthalenes needed more catalyst involved in the reaction and achieved the best consequence to some extent. When the TfOH addition amount was 0.8 wt%, the naphthalene conversion was 39.4%, and the selectivity of multi-butylnaphthalenes was only 7.6%. The amount of the catalyst was insufficient to convert the naphthalene to its multi-alkylation products. The conversion showed an upward trend with the extension of catalyst dosage that reached 98.5%, and the degree of alkylation deepened to make the selectivity of multi-butylnaphthalenes reached 82.9% when the TfOH addition amount was 3.2 wt%. This phenomenon illustrated that the increase in catalyst dosage could effectively provide more acidity and promote the transformation of mono- and di-butylnaphthalenes to multialkylation product [30].



**Figure 2.** Effect of the amount of catalyst on naphthalene alkylation reaction with *n*-butene. Reaction conditions: T = 60 °C; flow rate of *n*-butene = 20 mL/min; t = 40 min.

### 3.2.2. Reaction Temperature

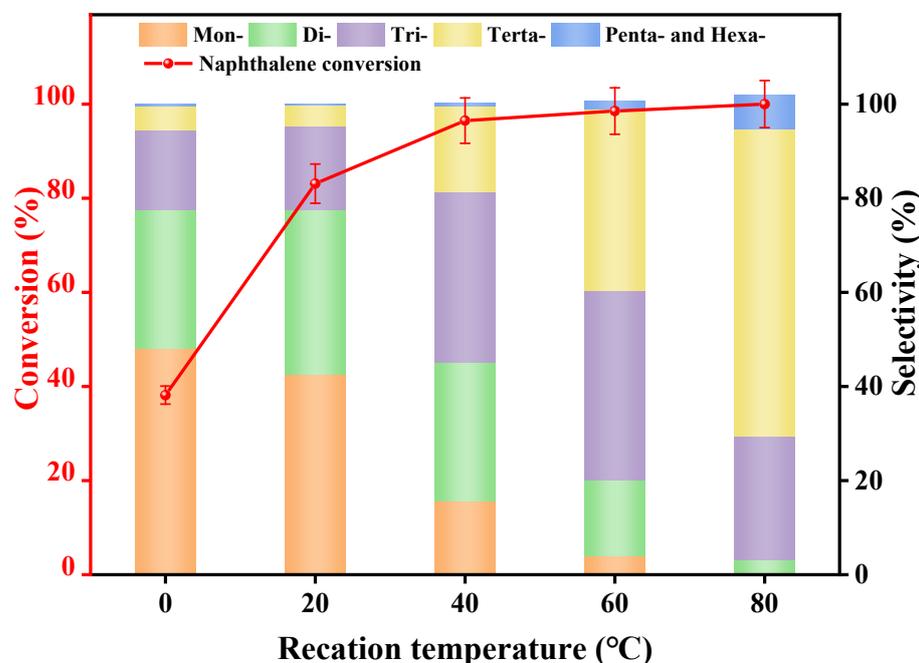
The effect of reaction temperature on the alkylation of naphthalene and *n*-butene was shown in Figure 3. At 0 °C, the conversion of naphthalene was only 38.2%, and the selectivity of multi-butylnaphthalenes was only 22.4%. A significant increase in the naphthalene conversion was observed from 0 °C to 60 °C, with the conversion increasing from 38.2% to 98.5%. Moreover, the reaction temperature had an obvious influence on the product distribution. In terms of the multi-alkylated product, the selectivity was increased from 22.4% to 80.6%. When the temperature was further increased to 80 °C, the selectivity of multi-butylnaphthalenes gradually increased to 98.8%, and the conversion of naphthalene was close to the value obtained at 60 °C. The multi alkylated products were thermodynamically more stable products, so the increase in temperature was beneficial to improve the selectivity of the multi alkylated product.

### 3.2.3. Flow Rate of *n*-butene

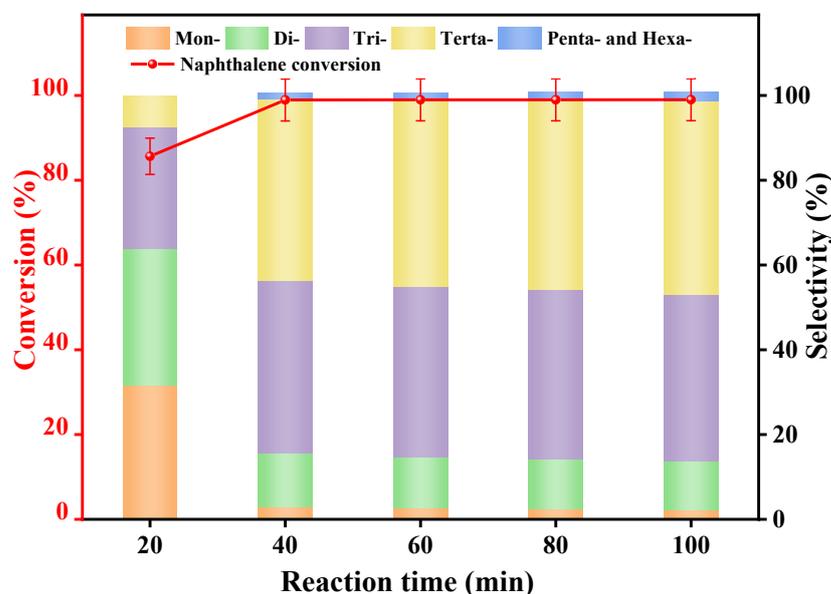
The stirring speed could influence the mass transfer process of the reaction [31]. As shown in Figure S4, the selectivity of multi-butylnaphthalenes increased from 33.0% to 80.0% as the stirring speed increased from 250 rpm to 500 rpm. There was no significant change with further increases. It was shown that the mixing of the reaction system and the potential for contact between the reaction phases were significantly enhanced by the high stirring speed.

The amount of the *n*-butene was studied by changing the *n*-butene flow rate on alkylation. From Figure 4, at 10 mL/min, the conversion of naphthalene was 97.5%, which was considered that naphthalene was able to react completely. Under this condition, the flow rate of *n*-butene was increased from 10–50 mL/min, more amount of the *n*-butene had a dramatic effect on the selectivity of the multi-butylnaphthalenes, but the conversion of naphthalene had no obvious change. The selectivity of multi-butylnaphthalenes was only 21.7% at an *n*-butene flow rate of 10 mL/min. The selectivity of multi-butylnaphthalenes reached more than 80.1% when the *n*-butene flow rate was greater than 20 mL/min. The product distribution of butylnaphthalenes gradually tended to balance as the flow rate of *n*-butene increased. It could be concluded that the addition of *n*-butene could promote

the process of multi-alkylation. This could be explained that the increase in the carbon ion concentration was favorable to the progress of the deep alkylation reaction. Unexpectedly, when the *n*-butene flow rate was high, excessive *n*-butene may lead to olefin polymerization catalyzed by TfOH under the certain reaction conditions [32]. Therefore, it could not only save the *n*-butene cost, but avoid possible side reactions at *n*-butene flow rate of 20 mL/min.



**Figure 3.** Effect of reaction temperature on the alkylation of naphthalene with *n*-butene. Reaction conditions: TfOH dosage = 3.2 wt%; flow rate of *n*-butene = 20 mL/min; *t* = 40 min.

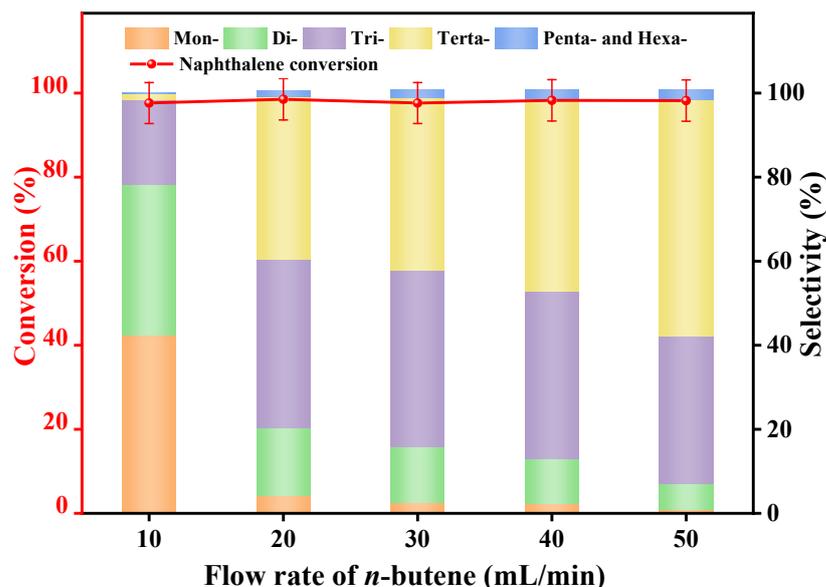


**Figure 4.** Effect of the flow rate of *n*-butene on the alkylation of naphthalene with *n*-butene. Reaction conditions: TfOH dosage = 3.2 wt%; *T* = 60 °C; *t* = 40 min.

### 3.2.4. Reaction Time

The influence of reaction time after the introduction of *n*-butene on the alkylation reaction was shown in Figure 5. Under the condition of 60 °C, the TfOH had high catalytic activity for the alkylation in the first 20 min, the conversion of naphthalene reached 85.7%

and the selectivity of multi-butylnaphthalenes accounted for 36.2%. Then, with the extension of reaction time, the conversion of naphthalene slightly increased from 85.7% to 98.9% at 40 min, and mono-butylnaphthalenes and di-butylnaphthalenes were gradually deeply alkylated to multi-butylnaphthalenes, and the selectivity of multi-butylnaphthalenes increased to 85.0% at 40 min [33]. However, it could be seen from Figure 5 that a further increase in the reaction time had only a slight influence on the selectivity of the reaction. It suggested that the continuous heating stirring reaction was carried out to ensure that the alkylation was sufficient and that no changes in the bulk phase composition were detected after 40 min as the reaction equilibrium was achieved.



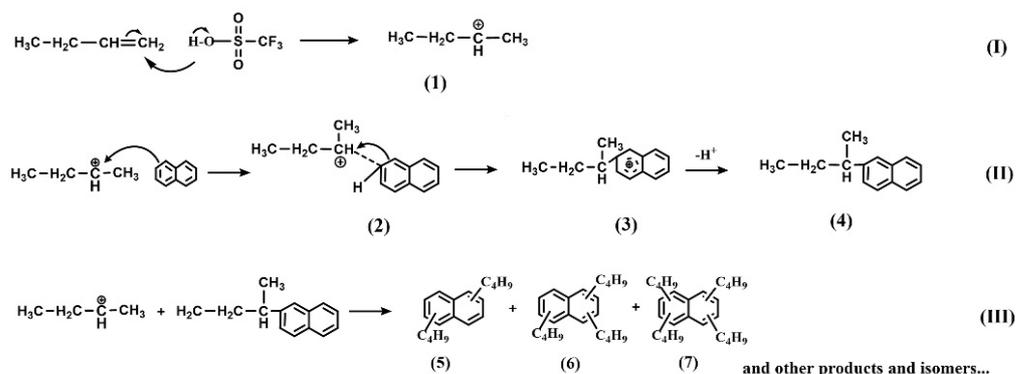
**Figure 5.** Effect of reaction time on the alkylation of naphthalene with *n*-butene. Reaction conditions: TfOH dosage = 3.2 wt%; T = 60 °C; flow rate of *n*-butene = 20 mL/min.

### 3.3. Catalytic Mechanism

According to the catalytic reaction results, the mechanism of alkylation of naphthalene with *n*-butene by using trifluoromethanesulfonic acid catalyst was proposed (Scheme 1). As shown in Scheme 2, the mechanism for alkylation of *n*-butene with naphthalene in the presence of TfOH involved interaction of the excess olefin with the TfOH to form a carbocation (1), which was essential for the initiation of the alkylation reaction. The carbocation attacked the  $\pi$  bond at different positions on the nucleus of the naphthalene to form unstable  $\pi$  complexes (2), then generating a stable  $\sigma$  complexes (3) through the transfer of carbocations. Finally,  $H^+$  dissociated from the  $\sigma$  complexes to generate mono-butylnaphthalenes (4) [34]. Then, mono-butylnaphthalenes continued to react with more carbonium ions to obtain the final multi-butylnaphthalenes (5, 6, 7) with more sidechains. With the increase in the number of side alkyl, the steric hindrance of naphthalene made it difficult to generate penta- and hexa- butylnaphthalenes, which only accounted for a small proportion of the product.

From Section 3.2, it was clear that the reaction conditions had a significant effect on the alkylation. The effects of different reaction conditions on the mechanism of alkylation were as follows. For example, increasing the catalyst dosage provided more amount of acid, which increased the active site and accelerated the reaction rate (I, II, and III) [30]. Additionally, promoting the alkylation of naphthalene and mono-butylnaphthalene when the reaction temperature was raised, and the thermal effect of the reaction decreased and promoted the multi-alkylated substitution (III) [35]. This was attributed to the greater activation energy required for the multi-alkylated substitution of naphthalene. For the *n*-butene flow rate, increasing the flow rate of *n*-butene enlarged the concentration of carbocations (1), and promoted the deep alkylation of mono- and di-alkylnaphthalene. At

the same time, the alkylation of naphthalene was a tandem reaction, in which naphthalene and *n*-butene rapidly produced a large amount of mono-butyl naphthalene at the beginning of the reaction (II). With the prolongation of the reaction time, *n*-butene further underwent deep alkylation reactions with naphthalene and mono-butyl naphthalene to obtain multi-butyl naphthalene (III).



**Scheme 2.** Reaction pathways of naphthalene with *n*-butene using TfOH to synthesize multi-butyl naphthalenes.

### 3.4. Physical and Chemical Properties of Multi-butyl naphthalenes

Through the investigation of reaction conditions, it was found that the different distributions of product obtained by controlling the reaction conditions. Thus, we synthesized two different compositions of alkyl naphthalene base oils MBN-1 (90.3% of both mono- and di-butyl naphthalenes) and MBN-2 (98.2% of multi-butyl naphthalenes) by adjusting catalyst dosage, and the products composition was shown in Table 1.

**Table 1.** Composition of multi-butyl naphthalenes oils.

Synthetic Oils	Proportion of Various Alkylated Products (%)				
	mono-	di-	tri-	tetra-	penta- and hexa-
MBN-1	59.5	30.8	8.4	1.3	0
MBN-2	0.4	1.4	36.5	57.8	3.9

The physicochemical properties of the two synthetic oils were analyzed on the reference sample of the commercial alkyl naphthalene base oil AN5, which was synthesized by alkylation of naphthalene and  $\alpha$ -olefin, and the product was mainly a mixture of mono- and di-alkyl naphthalenes: the specific data are shown in Table 2.

**Table 2.** Comparison of physicochemical properties of multi-butyl naphthalenes and AN5.

Properties	MBN-1	MBN-2	AN5
KV <sub>40</sub> (mm <sup>2</sup> ·s <sup>-1</sup> )	8.0	275.3	28.1
KV <sub>100</sub> (mm <sup>2</sup> ·s <sup>-1</sup> )	1.9	11.2	4.7
Density (g·cm <sup>-3</sup> )	0.9593	0.9230	0.9070
Flash point (°C)	140	173	222
Pour point (°C)	−59	−12.5	−51
Aniline point (°C)	17.1 *	18.6	32.0
Oxidative onset temperature (°C)	203.10	234.51	233.98

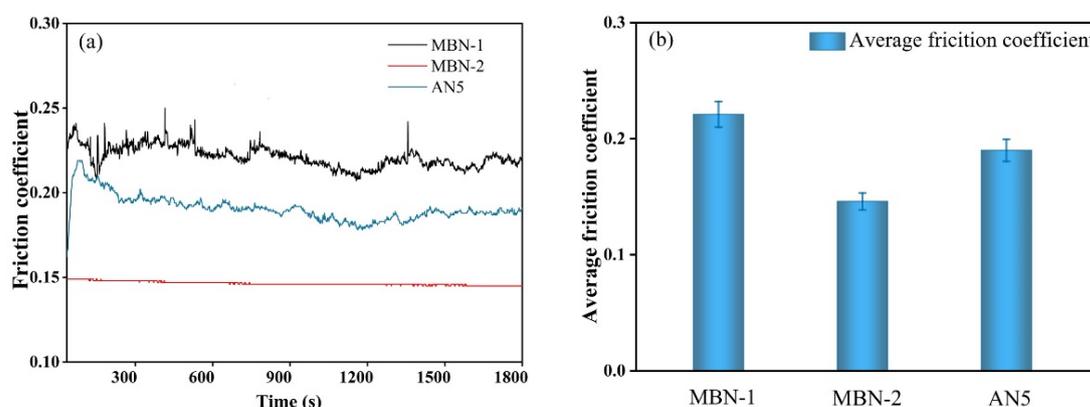
\*: Mixed aniline point.

The sample of both MBN-1 and MBN-2 base oils had high density, 0.9593 g·cm<sup>-3</sup> and 0.9230 g·cm<sup>-3</sup>, respectively. The viscosity of MBN-1 was lower than MBN-2 at both 40 °C and 100 °C, it may attributed to that MBN-1 had fewer alkyl side chains and weaker intermolecular forces than MBN-2 [36]. The pour point of MBN-1 was below −59 °C

and that of MBN-2 was  $-12.9\text{ }^{\circ}\text{C}$ . Since the aniline point of MBN-1 was lower than the crystallization temperature of aniline, the polarity of the sample was measured by testing its mixed aniline point. Thus, the polarity of MBN-1 was greater than that of MBN-2, because the increase in the number of alkyl side chains led to a decrease in the polarity of alkyl naphthalene product [37]. Moreover, the flash point of MBN-2 ( $173\text{ }^{\circ}\text{C}$ ) was higher than that of MBN-1 ( $140\text{ }^{\circ}\text{C}$ ), which was attributed to the more alky side chains on the naphthalene ring. The density at  $20\text{ }^{\circ}\text{C}$  and the oxidative onset temperature of MBN-2 were close to AN5. MBN-2 ( $18.6\text{ }^{\circ}\text{C}$ ) aniline point was lower than AN5 ( $32.0\text{ }^{\circ}\text{C}$ ), showing better additive solubility. At the same time, the viscosity of MBN-2 at both  $40\text{ }^{\circ}\text{C}$  and  $100\text{ }^{\circ}\text{C}$  were higher than AN5.

### 3.5. Tribological Performance

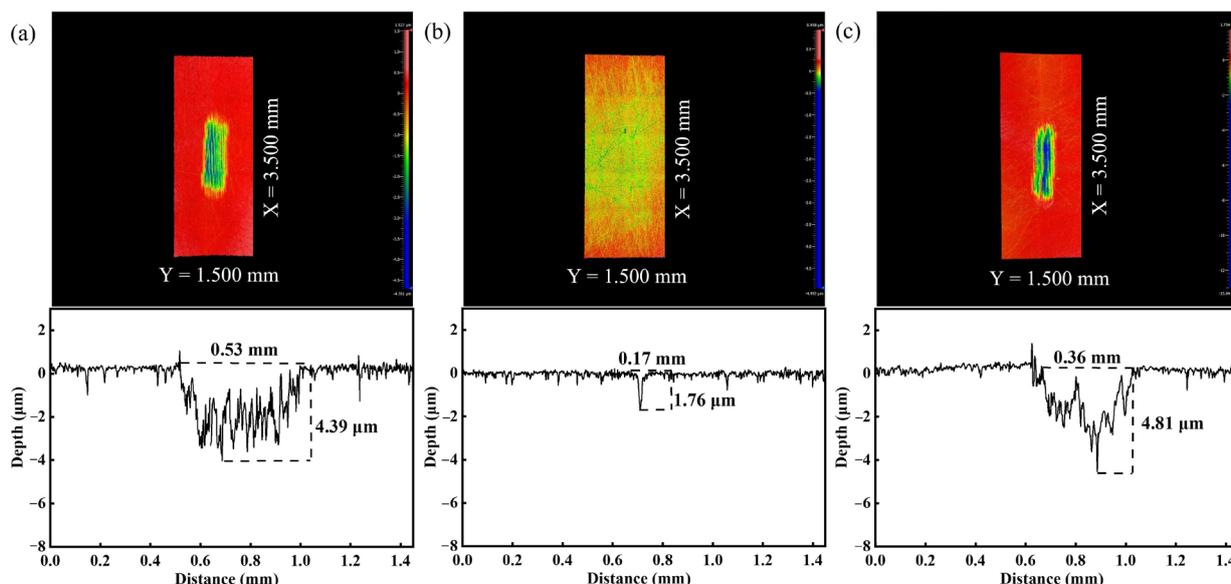
The composition of lubricating oil have a crucial influence on the friction performance and wear resistance [38]. In this experiment, the tribological properties of MBN-1, MBN-2, and AN5 were studied at sample volume of  $0.5\text{ mL}$ , temperature of  $25\text{ }^{\circ}\text{C}$ , frequency of  $50\text{ Hz}$ , load of  $100\text{ N}$ , stroke of  $1\text{ mm}$ , and duration time of  $1800\text{ s}$ . From Figure 6a, it displayed that MBN-1 showed a fluctuant friction curve and the high average friction coefficient of MBN-1 was  $0.221$ . The average friction coefficient of MBN-2 ( $0.164$ ) was lower than the of commercial AN5 ( $0.190$ ), as shown in Figure 6b. It can be found that MBN-2 showed lower friction reduction than commercial AN5. This was because the alkyl naphthalene was composed of the rigid structure of naphthalene ring and the flexible structure of alkane side chains. As the number of alkyl side chains on the naphthalene ring increased, the alkane content in the products increased. The MBN-2 was more stable in the friction process due to the flexible alkyl side chains intertwining to increase the deformable range, which improved the anti-friction performance of the alkylnaphthalene base oil [39]. The results indicated that the more side chains attached to naphthalene, the more stable the friction process and the lower the average friction coefficient.



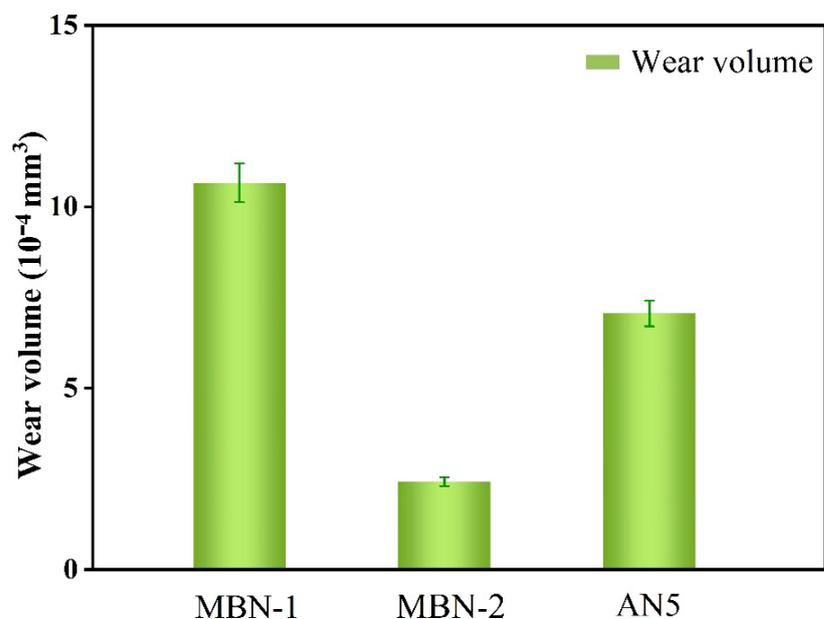
**Figure 6.** (a) The coefficient of friction curves; (b) The average friction coefficient lubricated by the synthetic oils and AN5.

The 3D images of the wear surface morphology (Figure 7) and the wear scar volume (Figure 8) of the steel disc lubricated by the synthetic oils are shown. MBN-1 showed the largest wear volume ( $10.66 \times 10^{-4}\text{ mm}^3$ ), due to its fluctuant friction curve, and had the largest wear scar width and depth ( $0.53\text{ mm}$  and  $4.39\text{ }\mu\text{m}$ , respectively). With the increase in the number of sidechains, the cohesive energy was enhanced between molecules, which was beneficial to strengthen its adsorption capacity on the surface of the steel plate, thereby reducing friction and improving load resistance [40]. Therefore, from the 3D images of the wear scar, MBN-2 had a shallow wear scar width ( $0.17\text{ mm}$ ) and the depth ( $1.76\text{ }\mu\text{m}$ ), and no obvious wear scars were observed on the friction surface; furthermore, the wear volume of MBN-2 was only  $2.43 \times 10^{-4}\text{ mm}^3$ . MBN-1 and AN5 had closed the number of side chains, but the wear volume of AN5 was  $6.73 \times 10^{-4}\text{ mm}^3$  showing a smaller wear volume

than MBN-1 because of longer side chains. Among them, the number and length of alkyl side chains on naphthalene affected its accumulation and adsorption capacity on the steel plate surface. The more side chains on the naphthalene ring enhanced the intermolecular interaction force, resulting in an increase in the viscosity of samples. This contributed to strengthen its adhesion ability on the surface of the steel plate, forming tough films that reduced the friction and increased the load-bearing capacity [41–43]. Therefore, with the increase in naphthalene alkylation degree, MBN-2 base oil exhibited better anti-wear performance than MBN-1 and commercial AN5.



**Figure 7.** The 3D profilometry microscope images of wear scars of steel disc for (a) MBN-1, (b) MBN-2 and (c) AN5.



**Figure 8.** The wear volume of the steel disc for the synthetic oils and AN5.

#### 4. Conclusions

Multi-butylnaphthalene oils were successfully synthesized by alkylation of naphthalene with *n*-butene with trifluoromethanesulfonic acid (TfOH) as catalyst. TfOH displayed an excellent catalytic performance with naphthalene conversion of 98.5%, and high selec-

tivity of 98.8% towards poly-butyl naphthalene under the optimal conditions of 3.2 wt% TfOH dosage, 20 mL/min *n*-butene flow rate, 60 °C, and 40 min. It had been found that the synthetic oils (MBN-2) with much more side-butyl on the naphthalene ring had higher viscosity, flash point, and oxidation onset temperature compared to that (MBN-1) with less sidechain on naphthalene. The tribological test results demonstrated that MBN-2 as lubricating base oil exhibited low friction coefficient and wear volume, displaying the comparable friction reduction and anti-wear performance to commercial alkyl naphthalene base oil AN5.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/lubricants11040156/s1>, Figure S1: Retention time of the alkylation of naphthalene with *n*-butene; Figure S2: The standard curve of naphthalene; Figure S3: The GC-MS results of the multi-butyl naphthalenes; Figure S4: Effect of stirring speed on the alkylation of naphthalene with *n*-butene.

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## Abbreviations

The following abbreviations are used in this manuscript:

TfOH	trifluoromethanesulfonic acid
GC	gas chromatograph
GC-MS	gas chromatography-mass spectrometry
Mono-	mono-butyl naphthalene
Di-	di-butyl naphthalenes
Tri-	tri-butyl naphthalenes
Tetra-	tetra-butyl naphthalenes
Penta-	penta-butyl naphthalenes
Hexa-	hexa-butyl naphthalenes
MBN-1	90.3% mono-/di-butyl naphthalenes
MBN-2	98.2% tri/tetra/penta/hexa-butyl naphthalenes

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