Characterization of Natural Ca-Bentonite Clays from Ebenebe in Anambra State, Nigeria, Impregnated with Ca(NO₃)₂, Zn(NO₃)₂ and KOH for use as Catalysts for Viscosity Reduction in Transesterification Reaction of Castor Oil

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ABSTRACT: Natural Ca-Bentonite from Ebenebe in Anambra State, Nigeria, was successfully impregnated with Ca(NO₃)₂, Zn(NO₃)₂ and KOH and further calcined under different conditions of temperature and time using standard methods. Both the natural and impregnated bentonite clays were characterized using Fourier Transform Infrared Spectroscopy (FTIR), X-ray Fluorescence Spectroscopy (XRF) and Scanning Electron Microscopy (SEM) and then applied as catalysts in transesterification reaction of refined castor oil. Viscosity reduction test was used to ascertain the best catalyst for the transesterification. FTIR spectra of the activated clay catalysts show the formation of new functional groups, as the intensity of the Al-O-H stretching group (3633 cm⁻¹) of the natural clay increased with slightly higher wavelengths of 3640 cm⁻¹, 3644 cm⁻¹, 3644 cm⁻¹, 3646 cm⁻¹ and 3656 cm⁻¹ for CaB₂, CaB₃, ZnB₂, KB₃Σ, and KB₀ catalysts respectively. XRF result identified the natural bentonite clay as Ca-bentonite clay with Ca-oxide having the most dominant component of 76.71%. XRF chemical compositions of the six activated Ca-bentonite clay catalysts when compared to the natural Ca-bentonite clay confirmed successful impregnation. The SEM images of all the prepared catalysts showed that impregnation and calcination changed the surface morphology of the natural clay. Finally, transesterification reactions of refined castor oil samples were done with 3% w/w natural and impregnated Ca-bentonite catalysts, methanol to oil ratio of 6:1, 2 hours reaction time and 65°C reaction temperature. Results obtained showed a descending order of catalyst viscosity reduction ability to be KB₃Σ > CaB₂ > KB₀ > NC'B > ZnB₂ > NaB₂.

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Keywords: Bentonite clay; Catalyst; impregnation; viscosity reduction; transesterification; castor oil

Clay minerals are small fragments of hydrous layer silicates. These important minerals with specific characteristics include montmorillonite, kaolinite, illite, vermiculite and chlorite (Ejikeme, 2017). Bentonite clay is a versatile class of smectite natural mineral, formed from alteration of siliceous glass – rich volcanic rocks and composed mainly of montmorillonite. It consists of 2:1 layer (Hwu et al., 2001), between which are exchangeable hydrated ions. A layer is composed of an octahedral sheet surrounded by two tetrahedral sheets (T.O.T) (Jahan et al., 2012). The basic unit of the octahedral layer is an octahedron which consists mainly Al³⁺ or Mg²⁺ surrounded by six oxygen atoms or hydroxyl groups. The tetrahedral layer has a tetrahedron as its basic unit and it contains one Si⁴⁺ at the centre with four oxygen atoms or hydroxyl groups at the corners. Bentonite was first used as a term to describe a particular highly colloidal, plastic clay, found near Fort Benton at the cretaceous beds of Wyoming, USA (Ujeneza, 2012; Kutlic et al., 2012). Bentonite clays are classified as Sodium (Na) -, Calcium (Ca) -, Potassium (K) - or Aluminium (Al) - bentonites depending on the dominant element (Ali et al., 2016). Ca – bentonite (a non-swelling type bentonite) and Na – bentonite (a swelling type bentonite) possess some physical properties that make them valuable to various industries (Olugbenga et al., 2013). Clay minerals and deposits generally vary in nature. Abdullahi et al., 2017, reports that samples from the same deposit tend to differ in the nature of exchangeable cations they contain and in the degree of chemical substitution within the smectite structure. Abdullahi et al., 2017, further reports that investigations by the Nigerian mining co-operation established the existence of bentonitic clay reserves of over 700 million tonnes in different parts of Nigeria.

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Activated clays have been used as catalysts for various reactions of industrial interests (Foletto et al., 2011, Didi et al., 2009). Reports on instrumental analysis of natural and activated clay samples for use as catalysts are available (Soetaredjo et al., 2011, Ali et al., 2016). Soetaredjo et al., 2011, impregnated bentonite with KOH, calcined and characterized it with Fourier Transform Infrared Spectroscopy. It served as a catalyst for transesterification of palm oil and gave favourable results. Different plant oils such as castor oil, various grades of shea butter (Ofoegbu-Chibuzo et al., 2022), palm oil, waste vegetable oil, jatropha oil, etc, can be utilized for transesterification reactions. Castor oil, an inedible oil, is a promising feedstock in transesterification reaction and thus, biodiesel production. Castor seed thrives very well on marginal land and though the oil has high viscosity, it has some advantages over other vegetable oils. Castor oil has more oxygen content and this enables more complete combustion (Conceicao et al., 2007). It also does not contain sulphur, thus, there is zero emission of oxides of sulphur (Conceicao et al., 2007). Again, castor oil has higher cetane number which depicts better quality of ignition (Ismail et al., 2016). Castor oil majorly contains hydroxylated fatty acids of ricinoleic acid, unlike other vegetable oils, and this makes it a better lubricity enhancer (Ramezani et al., 2010). Castor biodiesel is also proved to be the best fuel for cold weather as it has a very low cloud point and pour point (Ismail et al., 2016, Forero et al., 2004). It is however, usually blended with Petro diesel, because of its associated high viscosity and density. Transesterification performance varies inversely with viscosity, thus, castor oil with its high viscosity can be transesterified and viscosity reduction used to verify the transesterification performance of the natural and impregnated catalysts. Enwereamadi and Alamu, 2010, reported that viscosity is the basic parameter which reflects the extent of the transesterification reaction, as it directly relates to the methyl ester content. Thus, a significant change in viscosity with reaction indicates the removal of more of the heavy glycerine, which in turn signifies more complete reaction. In this study, natural Ca-Bentonite clay samples from Ebenebe in Anambra State, Nigeria, were impregnated with Ca(NO₃)₂, Zn(NO₃)₂ and KOH for use as catalysts for viscosity reduction in transesterification reaction of castor oil and characterized.

MATERIALS AND METHODS
Sample collection and preparation: Pulverized natural Ca-Bentonite, sourced from Ebenebe in Anambra State, Nigeria, was obtained through Mandid Nigeria Limited. The samples were rinsed with distilled water, filtered, and oven dried at 105°C for 24hours to remove water. The dried bentonite was crushed and sieved to obtain powdered bentonite.

Refined castor oil was obtained from Ayerton Saunders Co Ltd, Liverpool, UK. Analytical grade reagents were obtained.

Catalysts Impregnation: The catalyst impregnation was done following the method described by Ngobiri et al., 2020 as modified. 10g of natural calcium-bentonite (NCB) was first dispersed in 200ml of distilled water and stirred with magnetic stirrer for 10 minutes. At 65°C, a pre-dissolved amount of Ca(NO₃)₂ (2.5 g in 10 ml), Zn(NO₃)₂ (2.5 g in 10 ml) and KOH (2.5 g in 10 ml) was added separately to three separate samples of bentonite suspension. The reaction mixtures were stirred to a point of near dryness at the same temperature. The impregnated bentonite samples were dried in a laboratory oven for 24 hours at 110°C. The freshly dried clay samples were grinded into powder using a pestle and mortar and then stored in separate air tight containers for calcination.

Catalysts Calcination: Ca (NO₃)₂/Ca-bentonite catalyst was divided into sample A and sample B. Sample A was calcined in a tubular muffle furnace at a nitrate decomposition temperature of 650°C (Olivares, 2012) for 2hours to obtain CaO/Ca-bentonite catalyst sample A (CaB₂). Similarly, sample B was calcined at 650°C for 3 hours to obtain CaO/Ca-bentonite catalyst sample B (CaB₃). Zn(NO₃)₂/Ca-bentonite catalyst was divided into sample C and sample D. Sample C was calcined at 650°C for 2 hours to obtain ZnO/Ca-bentonite catalyst sample C (ZnB₂) while Zn(NO₃)₂/Ca-Bentonite catalyst sample D was calcined at 650°C for 3 hours to obtain ZnO/Ca-bentonite catalyst sample D (ZnB₃). KOH/Ca-bentonite catalyst was divided into sample E and sample F. Sample E was calcined at a temperature of 400°C for 5 hours (Soetaredjo et al., 2011) to obtain K₂O/Ca-bentonite catalyst sample E (KBₐ₀) and KOH/Ca-bentonite catalyst sample F was calcined at a temperature of 700°C for 2 hours to obtain K₂O/Ca-bentonite catalyst sample F (KB₇₀₀).

Characterization: FTIR Spectrophotometer (Shimadzu 8400S) was used for qualitative analysis (functional groups) of raw bentonite and impregnated bentonite samples. XRF Spectrophotometer (Bruker Penguian model) was used for qualitative and quantitative analysis (chemical compositions) of natural bentonite and activated bentonite catalyst samples. Scanning Electron Microscopy (Sputta Coater model QISORES) was used to study the surface morphology of the natural and prepared catalysts.

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Catalysts Transesterification Run: The sample catalysts (NCB, CaB₂, CaB₃, ZnB₂, ZnB₃, KB₄₀₀, & KB₇₀₀) were used for the transesterification of refined castor oil. This was carried out in a 250ml glass reactor equipped with a reflux condenser and magnetic hot plate stirrer set at 65°C. 3w/w% catalyst loading of the castor oil was added to a known volume of methanol and heated up to 65°C. The castor oil was heated up to 65°C and subsequently added to the reaction mixture of methanol to oil mole ratio of 6:1 under vigorous stirring. The transesterification reaction was carried out for two hours and the solution was thereafter centrifuged at 2500 rpm for 15 minutes in order to separate out the biodiesel from the catalyst and glycerol. After separation, 20ml of warm distilled water was gently poured and the mixture was gently stirred to avoid foam formation (Van, 2004). It was then left over night (12hrs) in a separation funnel to settle into water impurities phase and biodiesel phase. The biodiesel layer was then heated up to 105°C for 1hour to evaporate any remaining water molecule. After drying, the weight of biodiesel was taken while stored in a dark cupboard for further analysis.

Kinematic Viscosity Test: HK-265 kinematic viscosity apparatus from Liaoning Huake Petroleum Apparatus Science & Technology Co. Ltd was used to obtain the kinematic viscosities of the various transesterified samples at 40°C using ASTM D445-19 standard method.

RESULTS AND DISCUSSION

Table 1 summarizes the important functional groups assignment of NCB, as given in the FTIR spectrum of NCB. From the table, Al/Mg-O-H stretching (inter-octahedral) appeared at 3633 cm⁻¹, H-O-H stretching at 3450 cm⁻¹, Al-OH bending deformation (Al-O bending vibrations) at 918 cm⁻¹, Si-O stretching vibrations or (Si-O bending vibration) at 1119 cm⁻¹, and OH deformation vibration of water (bending vibration of groups in adsorbed water molecules) at 1689 cm⁻¹. According to previous report by Ritz et al., 2010, the first four assignments in Table 1 identify NCB as bentonite clay. Table 2, presents the important functional groups assignment from the FTIR spectra for the natural Ca-bentonite catalyst, NCB, for the CaO/Ca-Bentonite catalyst samples A and B (CaB₂, CaB₃), for the ZnO/Ca-bentonite catalyst samples C and D (ZnB₂, ZnB₃) as well as for K₂O /Ca-bentonite catalyst samples E and F (KB₄₀₀, KB₇₀₀).

Table 1: FTIR Assignments of natural Ca-bentonite clay (NCB)

| Wavelength (cm⁻¹) | Assignment                         |
|------------------|------------------------------------|
| 3633             | Al/Mg-O-H stretching (inter-octahedral) |
| 3450             | H-O-H stretching vibration         |
| 918              | Al-OH bending deformation (Al-O bending vibrations) |
| 1119             | Si-O stretching vibrations or (Si-O bending vibration) |
| 1689             | OH deformation vibration of water (bending vibration of groups in adsorbed water molecules) |

Table 2: Major FTIR Assignments of natural and activated Ca-Bentonite clay samples

| Bentonite | Wave length(cm⁻¹) | Assignment                  |
|-----------|------------------|-----------------------------|
| NCB       | 3633             | Al-O-H stretching (inter-octahedral) |
| CaB₂      | 3640             | Al-O-Ca                     |
|           | 1331             | NO₂                         |
|           | 1354             | NO₃                         |
| CaB₃      | 3644             | Al-O-Ca                     |
| ZnB₂      | 3644             | Al-O-Zn                     |
| ZnB₃      | 3644             | Al-O-Zn                     |
| KB₄₀₀     | 3640             | Al-O-K                      |
| KB₇₀₀     | 3644             | Al-O-K                      |

The activation of NCB with Ca(NO₃)₂ affected the structure of the bentonite by changing the intensity of Al-O-H stretching group and absorption band wavelength from 3633cm⁻¹ to 3640cm⁻¹ and 3644cm⁻¹ for CaB₂ and CaB₃ respectively. This indicates the presence of a new functional group Al-O-Ca and is in line with previous reports by Soetaredjo et al., 2011 and Ali et al., 2016. A medium peak at 1354cm⁻¹ indicates the presence of NO₃⁻ ion and the peak at 1331cm⁻¹ shows the presence of NO₂⁻ ion (Urresta-Aragon et al., 2012) for CaB₂ spectrum only. Thus, implying that 2 hours calcination time used for CaB₂ did not completely decompose the Ca (NO₃)₂ to CaO. Conversely, the NO₂⁻ ion peak and NO₃⁻ ion peak did not appear in the spectrum for CaB₃, which means that complete decomposition of Ca(NO₃)₂ to CaO at 3 hours calcination was achieved.

Similarly, activation of NCB with Zn(NO₃)₂ affected the structure of the bentonite by changing the intensity
of Al-O-H stretching group and absorption band wavelength from 3633cm\(^{-1}\) to 3644cm\(^{-1}\) and 3644cm\(^{-1}\) for ZnB\(_2\) and ZnB\(_3\) respectively. This indicates the presence of a new functional group Al-O-Zn and corresponds with previous reports by Soetaredjo et al., 2011; Ali et al., 2016. The absence of NO\(_3\) and NO\(_2\)- peaks in both spectra shows that the calcination temperatures of 650\(^\circ\)C at 2hours and 3hours respectively resulted to the complete decomposition of Zn(NO\(_3\))\(_2\) to ZnO. (Urresta-Aragon et al., 2012).

For the activation of NCB with KOH, the intensity of Al-O-H stretching group increased moderately at calcination temperature of 400\(^\circ\)C and greatly at calcination temperature of 700\(^\circ\)C. Also, a shift of absorption band of this group from 3633cm\(^{-1}\)to higher wave lengths of 3640cm\(^{-1}\) and 3644cm\(^{-1}\) for calcination temperatures of 400\(^\circ\)C and 700\(^\circ\)C respectively, indicates the presence of a new functional group (Al-O-K group) in the catalysts being investigated.

**Table 3: Chemical Composition of Natural and Impregnated Bentonite Samples**

|          | CaO   | SiO   | FeO\(_3\) | SO\(_3\) | Al\(_2\)O\(_3\) | K\(_2\)O | SrO   | TiO\(_2\) | Cl      | P\(_2\)O\(_5\) | ZnO |
|----------|-------|-------|-----------|----------|-----------------|---------|-------|----------|---------|-------------|-----|
| NCB      | 76.71 | 11.27 | 4.15      | 3.06     | 2.84            | 0.75    | 0.63  | 0.28     | 0.09    | 0.06        | BDL |
| CaB\(_2\)| 77.07 | 9.64  | 3.95      | 2.51     | 2.61            | 0.62    | 0.61  | 0.28     | 0.11    | BDL         | BDL |
| CaB\(_3\)| 80.05 | 9.71  | 3.65      | 1.97     | 2.56            | 0.56    | 0.53  | 0.26     | 0.11    | BDL         | BDL |
| ZnB\(_2\)| 70.91 | 8.61  | 3.77      | 2.20     | 3.43            | 0.63    | 0.57  | 0.27     | 0.09    | BDL         | 8.55 |
| ZnB\(_3\)| 70.69 | 9.11  | 3.74      | 2.16     | 3.59            | 0.49    | 0.55  | 0.22     | 0.10    | BDL         | 8.33 |
| KB\(_{400}\)| 64.52 | 8.84  | 3.39      | 1.03     | 1.82            | 19.49   | 0.53  | 0.19     | 0.09    | BDL         | BDL |
| KB\(_{700}\)| 67.56 | 5.66  | 3.53      | 1.54     | 1.07            | 19.56   | 0.54  | 0.29     | 0.12    | BDL         | BDL |

BDL – Below Detection Limit

Table 3 shows the XRF results (chemical compositions) of NCB, CaB\(_2\), CaB\(_3\), ZnB\(_2\), ZnB\(_3\), KB\(_{400}\), & KB\(_{700}\). From results in Table 3, the calcium oxide in CaB\(_3\) is higher than that of CaB\(_2\), thus, this XRF result confirms the FTIR result, that calcination at 650\(^\circ\)C for 3 hours decomposed Ca(NO\(_3\))\(_2\) completely to CaO when compared to calcination at 650\(^\circ\)C for 2 hours. On the other hand, ZnB\(_2\) and ZnB\(_3\) samples contain ZnO unlike the raw bentonite and other impregnated bentonite samples showing that these bentonites were successfully impregnated with Zn(NO\(_3\))\(_2\) and the calcination decomposed nitrates to oxides. However, calcination at 650\(^\circ\)C for 2 hours gave higher values suggesting that complete decomposition to zinc oxide was achieved within 2 hours. The K\(_2\)O compositions of KB\(_{400}\) (19.49) and KB\(_{700}\) (19.56) are higher than that of natural Ca- bentonite showing that impregnation occurred successfully. However, KB\(_{400}\) has a slightly higher composition compared to KB\(_{400}\). Scanning electron microscopy (SEM) identifies the surface morphology of a given sample. The SEM analysis of NCB, CaB\(_2\), CaB\(_3\), ZnB\(_2\), ZnB\(_3\), KB\(_{400}\), & KB\(_{700}\) gave images for the natural and impregnated catalysts, as shown in Figures 1 - 7.

**Fig 1:** Morphology of NCB

**Fig 2:** Morphology of CaB\(_2\)

**Fig 3:** Morphology of CaB\(_3\)

**Fig 4:** Morphology of ZnB\(_2\)

**Fig 5:** Morphology of ZnB\(_3\)

**Fig 6:** Morphology of KB\(_{400}\)

**Fig 7:** Morphology of KB\(_{700}\)
The SEM images of CaB$_2$ and CaB$_3$ in Figures 2 and 3 respectively, appear very similar, as the natural structure of NCB was destroyed by the impregnation and calcination to give homogenous particles (Naswir et al., 2013; Farias et al., 2015) with smoothed surfaces (Sharma et al., 2021). Thus, they have increased surface area which gives them room for good reactivity. However, CaB$_3$ morphology has more pores from its smoothed sponge-like surface structure compared to CaB$_2$ morphology, and this gives CaB$_3$ catalyst room for more reactivity and thus, higher viscosity reduction effect, as given in Table 4, compared to CaB$_2$ catalyst.

From the morphology of ZnB$_2$ in Figure 4, it can be seen that the natural structure of NCB was not destroyed by impregnation and calcination. ZnB$_2$ morphology shows more of large particles compared to NCB and ZnB$_3$ morphologies and this seems to explain its lower viscosity reduction as given in Table 4. The particles are also more compact than the particles of NCB and ZnB$_3$. The SEM image of ZnB$_3$ in Figure 5 shows that impregnation and calcination did not destroy the natural structure of NCB. The reduction of particle size from ZnB$_2$ to ZnB$_3$ as shown from Figures 4 to 5 occurred as a result of longer calcination time, which is 2 hours to 3 hours. Again, ZnB$_2$ morphology showed fewer large particles and more of small particles compared to NCB and ZnB$_3$. The particles are also clearly not compact. Thus, the SEM images seem to explain the higher viscosity reduction effect, given in Table 4, of ZnB$_3$ compared to NCB and ZnB$_2$. The natural structure of NCB grains can still be observed in the SEM image of KB$_{400}$ in Figure 6. However, it seems to have a more compact surface than the SEM image of NCB and thus, the surface area is decreased. The more compact surface could be caused by the aggregation of clay on K$_2$O on impregnation and calcination at 400°C and possibly, explains the much lower viscosity reduction effect of KB$_{400}$ given in Table 4, at mild reaction conditions. Again, although the XRF results showed relatively good content of K$_2$O in KB$_{400}$ compared to KB$_{700}$, the FTIR spectra of KB$_{400}$ showed much lower intensity and a lower wavelength. The K$_2$O seems to be more in the bentonite structure than on the surface, resulting to much lower viscosity reduction effect. An interesting occurrence can be observed from the surface characteristics of KB$_{700}$ in Figure 7. The natural structure of NCB grains has not only transformed to a smooth surface with pores, and thus, very large surface area but also the impregnated K$_2$O seems to interestingly form nano rod like (Saeed et al., 2021, Sharma et al., 2021) structures on the smooth surface of KB$_{700}$, thus, giving the catalyst a very high reactivity and thus, high viscosity reduction effect, as given in Table 4, at mild reaction conditions. Helwani et al., 2021, mentioned that calcination of KOH on cement clinker catalyst at 700°C results to high transesterification reactivity. The kinematic viscosity of transesterified castor oil using KB$_{300}$ heterogeneous catalyst (19.9 mm$^2$/s) at mild reaction conditions, is comparable to the results obtained by Silva, 2009, using homogenous KOH catalyst (20.3 mm$^2$/s) and Keera et al., 2018, using homogenous KOH catalyst (15.4 mm$^2$/s).

| Catalyst | Kinematic Viscosity at 40°C (mm$^2$/s) | Viscosity reduction (%) |
|----------|--------------------------------------|------------------------|
| Castor Oil | 189.482* | -                        |
| NCB | 69.050 | 63.56% |
| CaB$_2$ | 57.791 | 69.50% |
| CaB$_3$ | 42.841 | 77.39% |
| ZnB$_2$ | 107.576 | 43.23% |
| ZnB$_3$ | 61.188 | 67.71% |
| KB$_{400}$ | 135.401 | 28.54% |
| KB$_{700}$ | 19.907 | 89.49% |

*This served as a reference standard

Results of kinematic viscosity of the various transesterified castor oil samples using NCB, CaB$_2$, CaB$_3$, ZnB$_2$, ZnB$_3$, KB$_{400}$, and KB$_{700}$ catalysts are presented in Table 4. The kinematic viscosity of the end product served as indicator for the effectiveness of the catalyst in completing the ester conversion process (Enweremadu and Alamu, 2010; Brito et al., 2007; Felizardo et al., 2006; Al-Widyan and Al-Shyoukh, 2002; Canakci and van Gerpen, 1999). From the results obtained, there was a significant observed reduction in the kinematic viscosity for both the natural and activated bentonite clays used for transesterification. KB$_{700}$ catalyst gave the highest viscosity reduction of 89.49%, followed by CaB$_3$ with 77.39%, followed by CaB$_2$ with 69.50%, followed by ZnB$_3$ with 67.71%, followed by NCB with 63.56%, then followed by ZnB$_2$ with 43.23% and lastly by KB$_{400}$ with 28.54%. The activated bentonite catalysts, KB$_{700}$, CaB$_3$, and CaB$_2$, whose natural bentonite structures were destroyed by the calcination process to give a smooth and homogenous surface gave the most viscosity reduction (%), an indication that the activation of the bentonite clays proved useful.

**Conclusion:** Natural Ca-Bentonite (NCB) from Ebenebe in Anambra State, Nigeria, was successfully impregnated with Ca(NO$_3$)$_2$, Zn(NO$_3$)$_2$ and KOH, and calcined at various time and/or temperatures to produce six different catalysts (CaB$_2$, CaB$_3$, ZnB$_2$, ZnB$_3$, KB$_{400}$, and KB$_{700}$). KB$_{700}$ proved to be very good for the purpose of transesterification reaction of refined castor oil at mild reaction conditions. Obtained results showed the descending order of catalyst

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viscosity reduction ability to be KB_{200} > CaB_{3} > CaB_{2} > ZnB_{3} > NCB > ZnB_{2} > KB_{400}.

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